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Development of CZTSSe Thin Film Solar Cells with Inclusions of Selenium in the Precursor Stack

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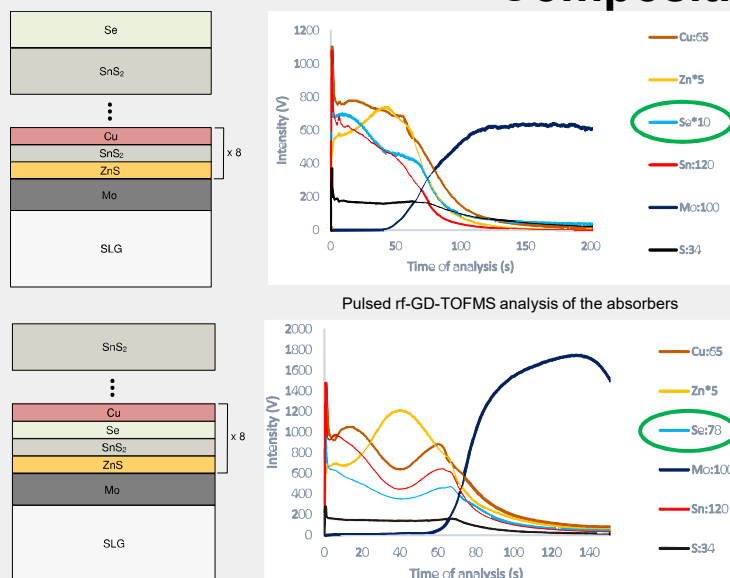
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Abstract

Cu₂ZnSn(S_xSe_{1-x}) (CZTSSe) solar cells were produced by sputtering of a precursor stack, where the element Se was thermally evaporated onto the precursors in two different configurations, followed by annealing in H₂S using an RTP furnace. The absorbers produced exhibited blisters. The S/(S+Se) profile in each configuration and blister formation investigations in CZTS are presented.

Composition Grading



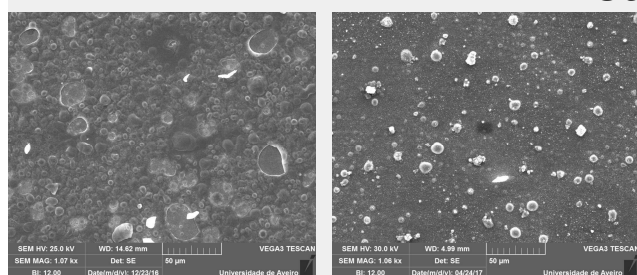
Se on top of precursors

The composition profile reveals that there is a vertical gradient of Se, while the S profile remains nearly constant. This is consistent with a profile resulting from diffusion of Se from the surface into the absorber during annealing. However, the grading was low, with the S/(S+Se) ratio varying from 1 to 0.9 (back to front).

Se within the precursors

The composition now shows a more uniform Se content. This suggests that this precursor scheme can be used to tune the S/(S+Se) ratio, and variations from 1 to 0.5 were achieved. Custom vertical gradients could be possible by tuning the thickness of the Se layer within each precursor period.

Blister Investigation



0.5 °C/s

0.2 °C/s

Heating Rate

It was found that blister formation is closely related to the heating rate during the annealing step. Very low (< 0.2°C/s) and very high (> 5°C/s) heating rates were found to almost eliminate blistering, while intermediate led to severe blistering.

Competing phenomena?

Volatilization Losses

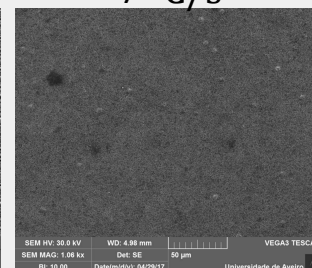
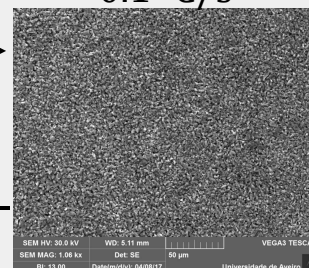
VS

CZTS Formation

A very fast annealing has low volatilization losses, while a very slow annealing hinders blister growth dynamics due to weaker temperature gradients.

0.1 °C/s

7 °C/s



Conclusion

The Se depth profile hints that a bandgap grading is possible using the proposed precursor configurations.

Blistering was shown to be strongly dependent on the heating rate during annealing, and two different blister-free regions were identified. An explanation based on the competition between volatilization losses and CZTS formation is proposed to explain the results.